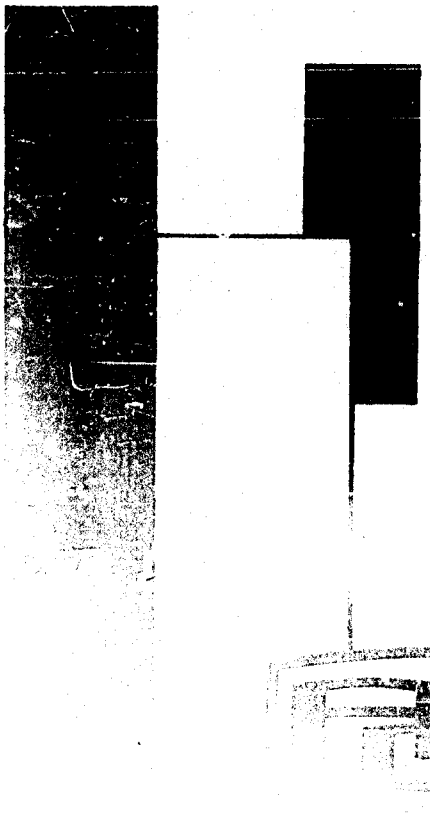
A.O. Smith CORPORATION



MILWAUKEE 1, WISCONSIN • UPTOWN 3-3000

A.O. Smith CORPORATION

April 15, 1963

Gentlemen:

Progress Report #14 on Glass Surface Chemistry for Glass Fiber Reinforced Plastics for the period April 1 through April 30, 1963 is enclosed.

Some interesting deductions have been made from the bond life studies. The bond strength testing is still somewhat erratic, but we believe significant results will be obtained. It appears that a higher, faster cure cycle increases the bond strength in our particular test.

Very truly yours,

A. O. SMITH Corporation

F. W. Nelson, Director
Ceramic Research and Development

FWN:mk

PROGRESS REPORT #14
on
GLASS SURFACE CHEMISTRY FOR GLASS FIBER REINFORCED PLASTICS
for the period
April 1, through April 30, 1963

I. Summary

Owens-Corning's HTS finish on E glass continued to compare favorably to successful coupling agents, such as A-1100. The HTS samples have been on flat plate test in 190°F water for 35 days. In miscellaneous bond life studies, it was found that (1) a 190°F 100% R.H. environment appeared more severe than immersion in 190°F water, (2) synthetic sea water behaved similar to distilled water, and (3) extrapolations of bond life data indicated that room temperature water would require an estimated 45 years to cause complete debonding of A-1100 treated E glass laminates.

Additional evidence was gathered to demonstrate the effect of specially constituted E glass surfaces on the strength of glass-epoxy systems. Impregnating E glass surfaces with sodium created a weak interfacial layer that failed prematurely, probably because of excessive shrinkage stresses in the resin. Treatment of this alkali-rich glass surface with A-1100 was helpful, but the addition of chopped E glass fibers to the resin in an attempt to reduce shrinkage and promote strength was of no benefit. As expected, no discernible effect resulted from treating the alkali-deficient glass surface with A-1100 because failure was always in the material; and not in the interface.

To date, the highest strength of any butt-joint chain specimen that failed in the resin was 6700 psi. Tensile specimens of Epon 828 (CL) in dog bone shape failed at 13,000 psi. This difference in strengths was believed due to the special shape of the resin column required to concentrate the stress at the glass-resin bond. However, epoxy resin cast into rods and machined to the shape of the butt-joint chain specimens failed at 12,600 psi. Thus, the strength difference was not due to the special stress-concentrating shape. It was also found that a higher curing temperature, shorter time, and faster cooling increased the glass-resin bond strength. It would appear that residual tensile stresses in the resin is the significant variable that requires control.

It is anticipated that the bond strength testing will be completed in May.

II. Bond Life Studies by the Flat Plate Test

Table I summarizes the present flat plate testing. After 35 days, three of the four HTS samples showed signs of degradation, but none have failed. Exposure of A-1100 treated chemically cleaned E glass flat plate specimens to a 100% R. H. atmosphere appeared more severe than exposure to water (73 days compared to 186 days). No significant difference was found between synthetic sea water* and distilled water with respect to debonding epoxy resin from untreated chemically cleaned glass surfaces (both about 5 hours or less).

Debonding from untreated glass by water at room temperature occurred after 61 days, which is about 250 times longer than at 190°F. This data can be used to extrapolate the bond life of A-1100 treated chemically cleaned E glass in room temperature water, assuming the effect of temperature is linear:

(1) $\frac{x}{b} \cong a/c$ where,

x = bond life of A-1100 treated glass surface in room temperature water, in days

a = bond life of A-1100 treated chemically cleaned as-cast glass surface in 190°F water, in days

b = bond life of untreated chemically cleaned as-cast glass surface in room temperature water, in days

c = bond life of untreated chemically cleaned glass surface in 190°F water, in days

Thus, from Table I.

(2) $\frac{x}{61} \cong \frac{186}{(5/24)} = 54,500$ days (approx. 150 years)

Since in a laminate the glass fiber surface more near similates a degassed glass surface, another calculation predicts that the A-1100 treated degassed glass surface would fail in room temperature water after about 45 years. This same calculation will be applied to HTS finish glass as soon as testing is completed.

It would seem unlikely that water exposure at room temperature degrades the laminate by causing debonding. The possibilities would be if the glass fibers were incompletely covered with A-1100(1), or if the water was allowed to wick along the individual glass fibers in a filament or roving(2).

*See Table II for formula.

III. Bond Strength Studies by the Butt-Joint Chain Method

A. Correlation of Cure Schedules

Figure 1 shows the effect of resin curing procedures on the bond strength. Increasing the curing temperature from 290 to 350°F, decreasing the cure time, and fan cooling the specimens in the air-circulating oven increased the bond strength. This result was established with 95% confidence. Table III summarizes the two cure procedures.

In apparent disagreement, McGarry[3] used a different test method and found that a polyester resin required an optimum cure temperature (about 150°F) for maximum bond strength. Nevertheless, it would be interesting to see whether glass fiber laminate strength could also be improved by the higher cure temperature, shorter cure time, and faster cooling.

B. Addition of Chopped E Glass Fibers to Resin

Figure 2 shows the effect of adding chopped E glass fibers to the resin in an attempt to reduce shrinkage and promote strength. Figure 2 indicates that no apparent benefit resulted from this procedure since glass, resin, and pre-test failures were not prevented. However, it is felt that glass fibers could be of definite benefit if allowed to directly contact the glass surface to be bonded, but this modification would not maintain the desired resin-to-glass interface.

C. Bonding to Alkali-Deficient E Glass

Figure 3 shows the variation of bond strength due to acid leaching the E glass. No failures occurred in the bond, defined as a mirror interface on the glass after removal of the resin. Rather, failures generally occurred in the glass. This result agrees with that previously reported[4]. Treatment with A-1100 did not appear to affect the strength of the alkali-deficient glass-epoxy system because failure was in the material, and not in the interface containing the A-1100.

D. Bonding to Alkali-Rich E Glass

Figure 4 shows the variation of bond strength due to exposing E glass to sodium vapors. Without treatment of coupling agent, all failures were pre-test and occurred at the interface. Apparently, the sodium created a weak interface that could not withstand the

shrinkage stresses of the resin and the necessary mechanical handling to enable testing. Treatment with A-1100 was effective in improving the strength of the glass-resin interface. However, the bond strength was still consistently lower than the bond strength of the chemically cleaned glass surface. This testing indicated that the presence of alkali at the interface definitely impaired bond strength.

E. Relation of Stress-Concentration Shape to Resin Strength

It was previously reported that the tensile strength of Epon 828 (CL) was about 13,000 psi[5]. However, the maximum strength of a butt-joint chain specimen which caused failure in the resin was only about 6700 psi. A possible explanation for this difference was based on the special shape of the resin column bonded to the glass surface. This shape was designed to concentrate the stress at the bond, thereby promoting bond failures.

To evaluate the shape factor, epoxy resin was cast into rods and machined to the form of the butt-joint chain specimen. For 5 specimens, the average tensile strength was 12,600 psi (σ = 3,600 psi). The range was from 11,200 to 15,300 psi. This strength correlated with the tensile strength of the resin in the dog bone shape. Thus, the stress-concentration-shape did not decrease the measured strength of the resin.

It is presently believed that the main cause for this difference of 6700 psi compared to 12,600 is due to residual tensile stresses in the resin. A possible way to further evaluate this effect would be to prepare butt-joint chain specimens that bond resin to resin. However, it has also been observed that the magnitude of the resin failures appeared dependent on the type of glass surface. When all glass surfaces have been evaluated for glass-epoxy strength, it is planned to compare the resin failures for each glass surface.

References:

(1) Sterman, S. and H. Bradley, "A New Interpretation of the Glass-Coupling Agent Surface Through Use of Electron Microscopy," S. P. I. preprints Section 8-D, page 1 (Feb., 1961).

(2) Anderson, A., "Comments on Paper 20-A" 18th S. P. I. Preprint (Feb. 1963).

(3) McGarry, F. and L. Broutman, "Glass-Resin Joint Strength Studies," Modern Plastics, page 161 (Sept. 1962).

(4) Progress Report #12.

(5) Progress Report #5.

TABLE I

BOND LIFE STUDIES BY FLAT PLATE TEST
Days to Failure Determined Visually

Type of Surface	Treatment	Days to Failure
AS-CAST E GLASS		
Chemically cleaned	None	1
Chemically cleaned	A-1100	186
Contaminated	None	1
Contaminated	A-1100	186
Contaminated	HTS	35*
Alkali-deficient (prepared in air)	None	106*
Alkali-deficient	None	230
Alkali-deficient	A-1100	226*
Alkali-rich	None	12
Alkali-rich	A-1100	49
Lightly sandblasted	None	7
Lightly sandblasted	A-1100	205*
Cleaved in resin	None	1
Degassed	None	1
Degassed	1/2% A-1100	55
Degassed	10% A-1100	80
Degassed	1/2% Z-6040	229*
As-Cast (Annealed)	None	1
Chemically cleaned, heated to 190°F before resin applied.	None	1
Chemically cleaned, exposed only to 100% R. H. at 190°F	None	1
Chemically cleaned, exposed only to 100% R. H. at 190°F	A-1100	73
Chemically cleaned, exposed to water at room temperature	None	61
Chemically cleaned, exposed to synthetic sea water at 190°F	None	1
OPTICALLY FLAT E GLASS		
Chemically cleaned (marbles)	None	1
Chemically cleaned (marbles)	A-1100	18
Chemically cleaned (repeat)	A-1100	50*
Alkali-deficient (marbles)	None	11
Alkali-deficient (marbles)	A-1100	54*
Alkali-deficient	None	44*
Alkali-deficient	A-1100	44*
Lightly sandblasted (marbles)	None	51*
Lightly sandblasted (marbles)	A-1100	51*

*Still on test.

TABLE II

SYNTHETIC SEA WATER*

	Grams Per Liter of Water
Sodium chloride	24.5366
Hydrated Magnesium Chloride	11.1181
Sodium Sulfate	4.0944
Calcium Chloride	1.1583
Potassium Chloride	0.6925
Sodium Bicarbonate	0.2010
Potassium Bromide	0.1028
Boric Acid	0.0273
Hydraded Strontium Chloride	0.0420
Sodium Floride	0.0030

Sodium Carbonate was added to adjust the pH to 8.2.

*Navy specification, Kure Beach, North Carolina, June 7, 1946.

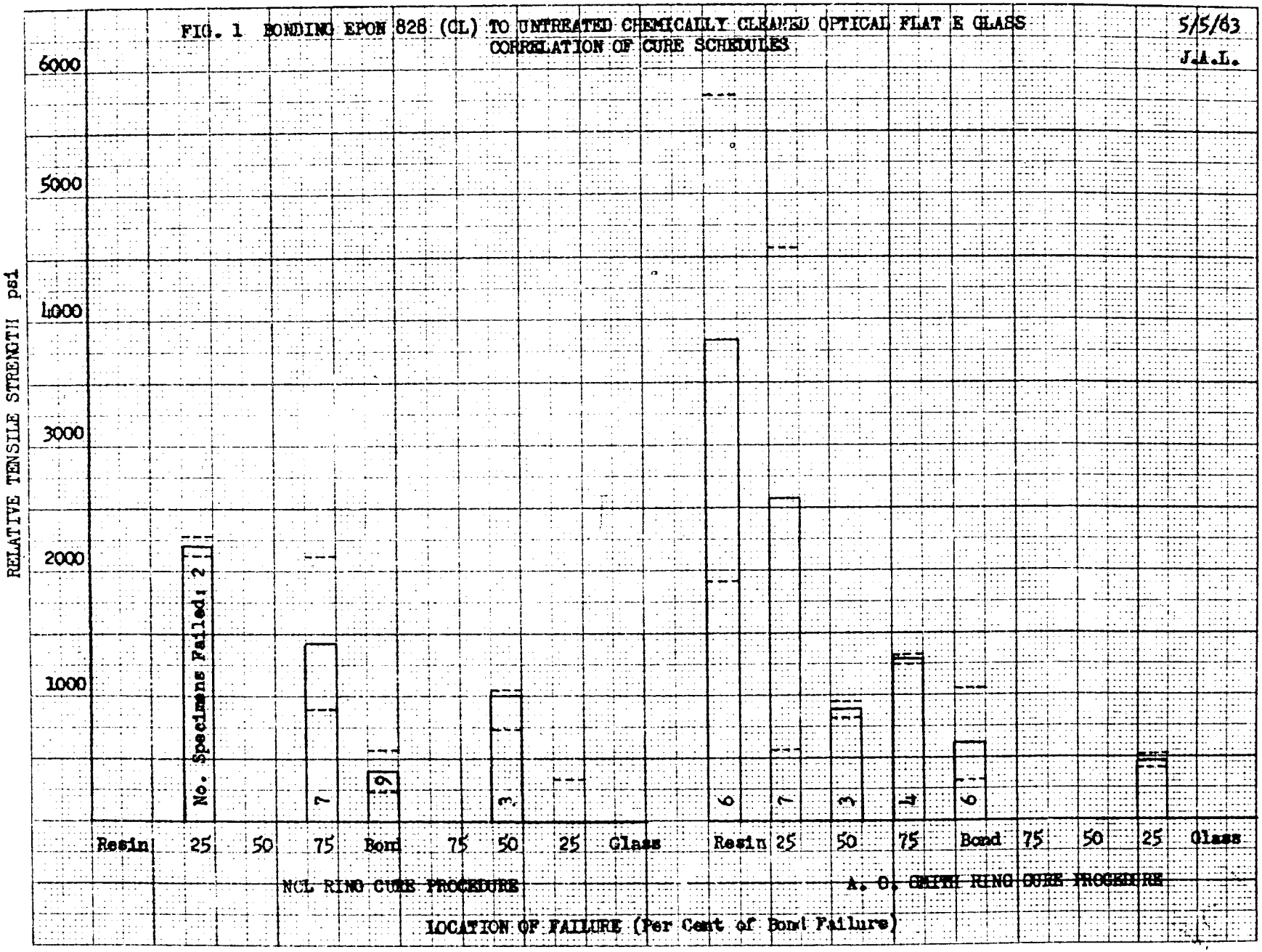
TABLE III

RESIN CURING SCHEDULES FOR BOND SPECIMENS

Present Short Cure Procedure		NOL Ring Cure Procedure	
Time (hrs.)	Temp. °F	Time (hrs.)	Temp. °F
1	250	16	Rm
1	350	2	140
fast-cool		2	190
		2	290

FIG. 1 BONDING EPON 828 (CL) TO UNTREATED CHEMICALLY CLEANED OPTICAL FLAT E GLASS
CORRELATION OF CURE SCHEDULES

5/5/63
J.A.L.



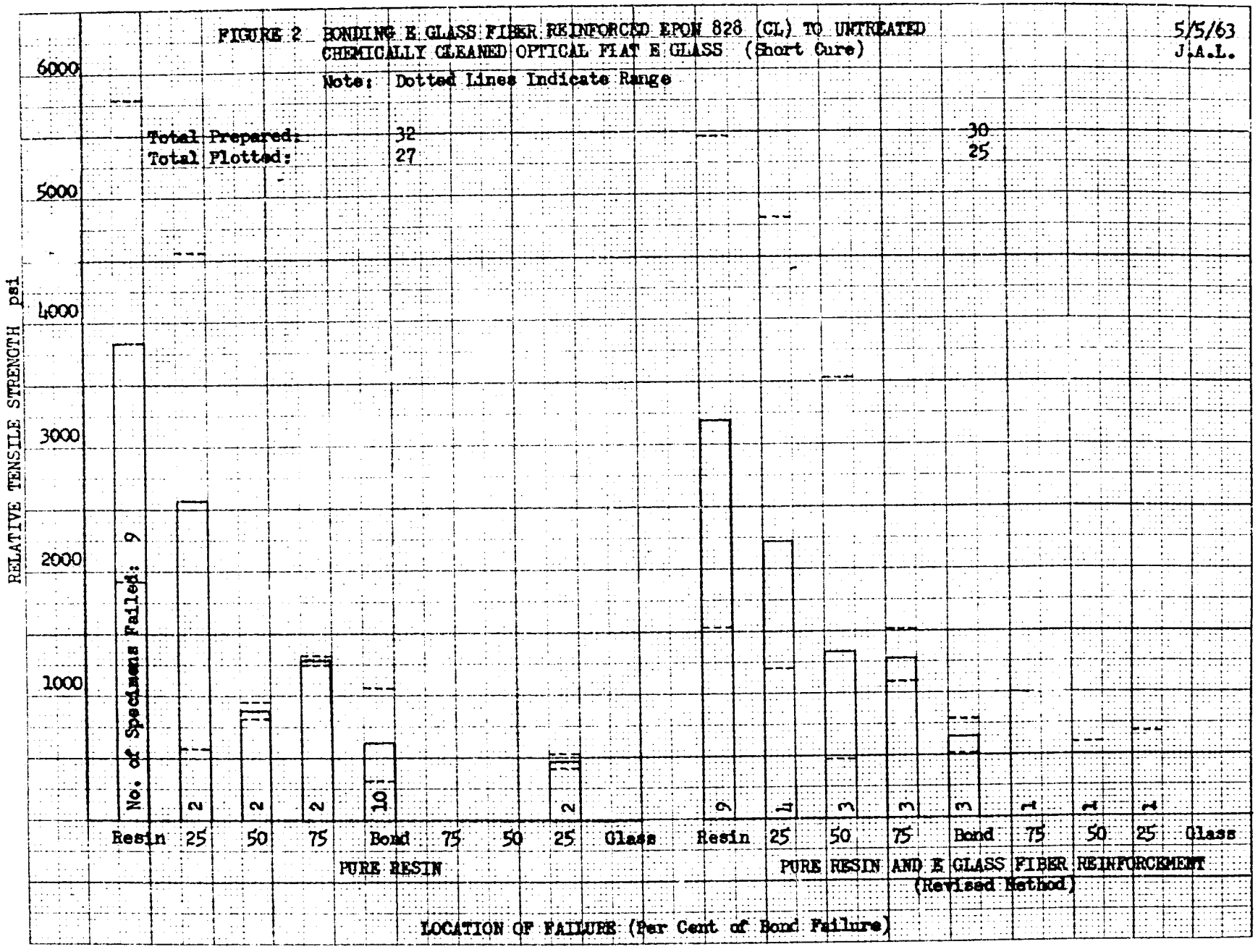
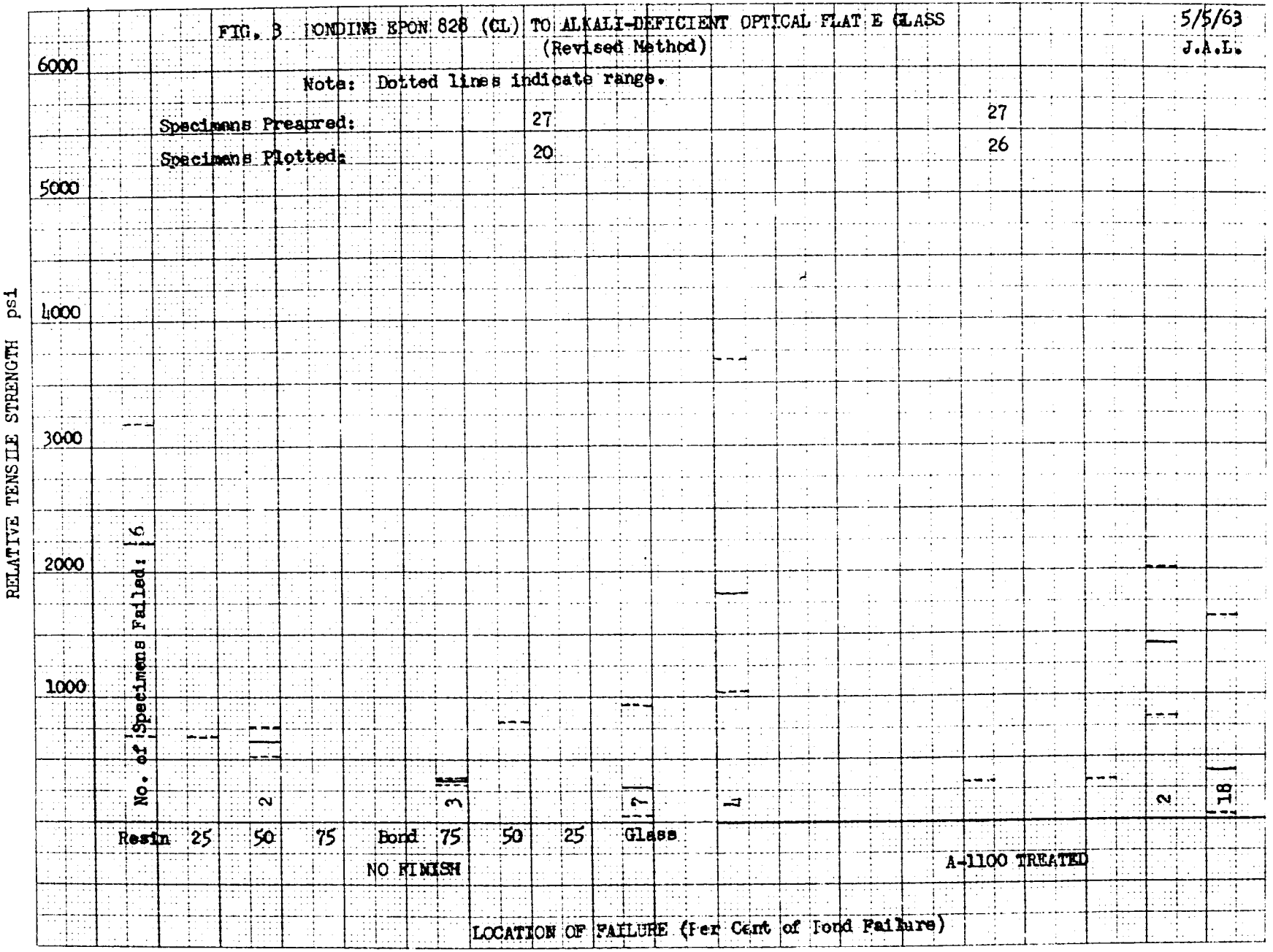


FIGURE 2 BONDING E GLASS FIBER REINFORCED EPON 828 (CL) TO UNTREATED CHEMICALLY CLEANED OPTICAL FLAT E GLASS (Short Cure)
5/5/63
J.A.L.
Note: Dotted Lines Indicate Range
Total Prepared: 32
Total Plotted: 27
30
25
RELATIVE TENSILE STRENGTH psi
6000
5000
4000
3000
2000
1000
No. of Specimens Failed: 9
2
2
2
10
2
9
4
3
3
3
1
2
2
Resin
25
50
75
Bond
75
50
25
Glass
Resin
25
50
75
Bond
75
50
25
Glass
PURE RESIN
PURE RESIN AND E GLASS FIBER REINFORCEMENT
(Revised Method)
LOCATION OF FAILURE (Per Cent of Bond Failure)

FIG. 3 BONDING EPON 828 (CL) TO ALKALI-DEFICIENT OPTICAL FLAT E GLASS (Revised Method)

5/5/63
J.A.L.



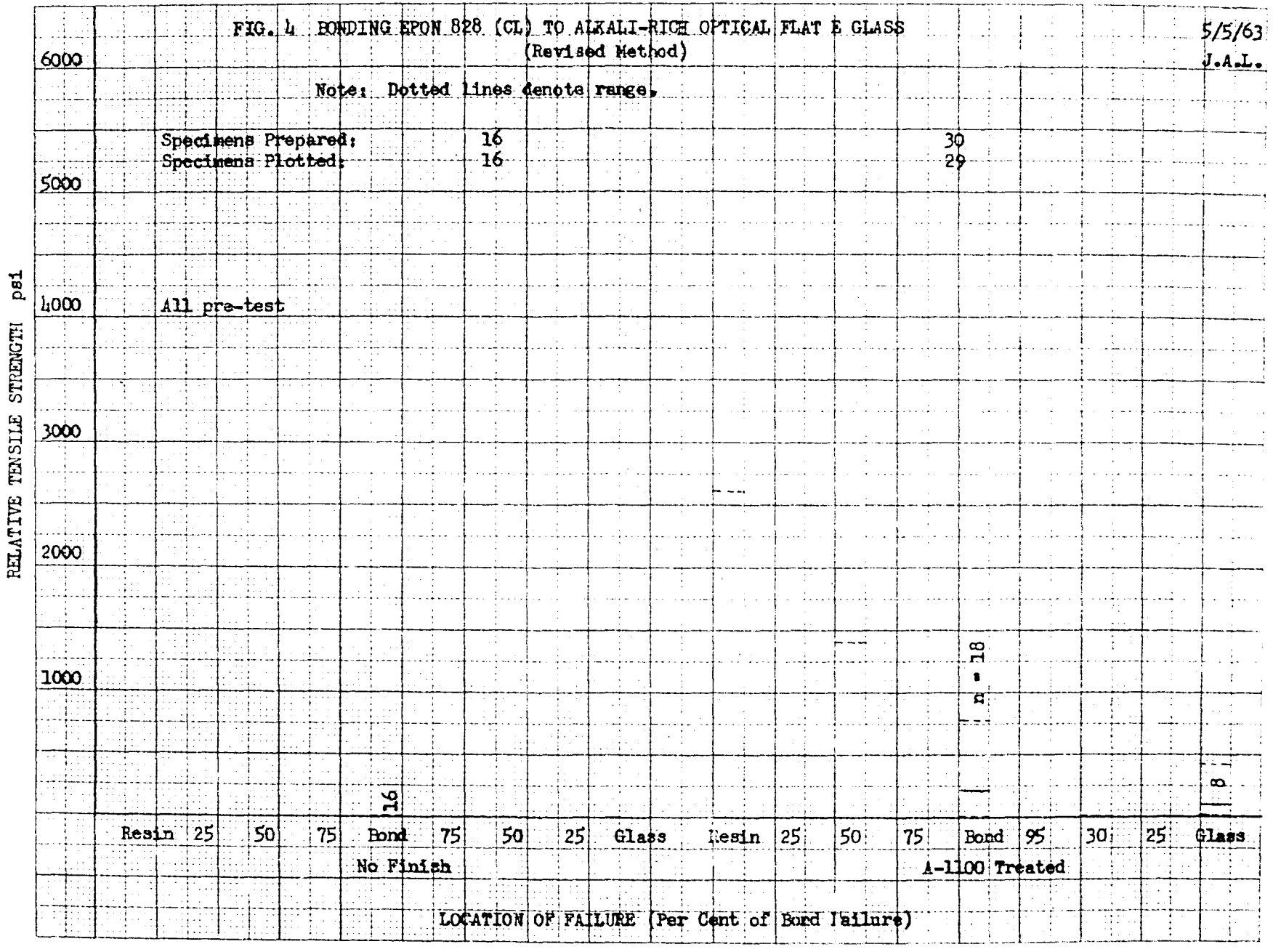


FIG. 4 BONDING EPON 828 (CL) TO ALKALI-RICH OPTICAL FLAT E GLASS
(Revised Method)
5/5/63
J.A.L.
Note: Dotted lines denote range.
Specimens Prepared: 16 30
Specimens Plotted: 16 29
All pre-test
RELATIVE TENSILE STRENGTH psi
6000
5000
4000
3000
2000
1000
16
18
8
Resin 25 50 75 Bond 75 50 25 Glass Resin 25 50 75 Bond 95 30 25 Glass
No Finish
A-1100 Treated
LOCATION OF FAILURE (Per Cent of Bond Failure)